Experimental Analysis and Thermodynamic Calculation of the Structural Regularities in the Fusion Diagram of the System of Alloys Al-Mg-Si

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Sections of the phase diagram Al-Mg-Si with up to 35 at.% magnesium and 35 at.% silicon are constructed. The thermodynamic calculation and experimental analysis have shown that the conode of three-phase eutectic equilibrium L $\Leftrightarrow$ α-Al + Mg_2Si, corresponding to the maximum temperature of eutectic transformation, does not coincide with the stoichiometric cross section between Al and Mg_2Si in the Al-Mg-Si ternary system, but rather occurs toward the magnesium-rich side of the ternary diagram. A polythermal cross section, corresponding to this conode, has been constructed. Concentration-temperature parameters of the univariant eutectic transformation L $\Leftrightarrow$ α-Al + Mg_2Si, as well as the boundaries of the domain of existence of alloys crystallizing with the formation of only two phases, namely, α-Al and Mg_2Si, were determined. Modeling of phase equilibria involving solid and liquid phases in the ternary system Al-Mg-Si was carried out. The topology of the phase diagram is stable against a wide range variation of the adjustable parameters; the inherent form of the diagram seems well established. The reasons for this are discussed.

1. Introduction

The Al-Mg-Si system is one of the prospective ternary systems for development of the advanced aluminum-based cast alloys [1984Nak, 1979Mon]. The phase diagram of this system features the existence of a quasi-binary section[1] between the Al-based fcc solid solution and the Mg_2Si silicide. The eutectic alloy (α-Al + Mg_2Si) located on this section has the maximum melting temperature (T_{max} = 595 °C) and zero melting range. It contains ~13 vol.% Mg_2Si. In the development of new alloys, a knowledge of the exact position of the quasi-binary section in the phase diagram is often required.

Until now, the calculations of the fusion diagram of the Al-Mg-Si system have been performed by several groups using rather complex thermodynamic models of liquid and solid solutions and the three-particle interaction parameters [1997Feu, 1992Cha, 1986Lüd, 1987Lac]. A detailed thermodynamic calculation of the aluminum-rich corner of the fusion diagram in this system was performed in [1997Feu]. The results suggest that the position of the quasi-binary section does not coincide with the stoichiometric section Al-Mg_2Si. The authors also reported experimental data for several polythermal sections (at 95, 90, 85, and 80 mass% Al), which confirm their calculated results. However, the position of the area of binary crystallization of alloys and the concentration-temperature parameters of monovariant eutectic transformation L $\Leftrightarrow$ α-Al + Mg_2Si have not been found. Thus, the present thermodynamic modeling of this system was undertaken to determine the nature of the fusion diagram and the level of stability of the regularities of eutectic transformation (L $\Leftrightarrow$ α-Al + Mg_2Si) against the variations in thermodynamic parameters describing the phase equilibria in this class of alloys.

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[1] On the quasi-binary section of the ternary phase diagram, a conode triangle describing the three-phase equilibrium among the liquid melt, solid solution, and stoichiometric compound degenerates into a direct line (conode), on which all three phases are in equilibrium at constant temperature [1978Zak].

2. Thermodynamic Analysis

The thermodynamic calculation of phase equilibria in the system under consideration was performed within the framework of a modified quasi-chemical model [1966Smi], assuming a linear temperature dependence of the interaction parameters of the atomic pairs (W^f_{ij}). This model is advantageous for its simplicity as well as for the fact that its parameters have a meaning of interaction energies between all kinds of atom pairs and thus can be determined by various methods including the *ab initio* calculations. Optimization of parameters was done by recurrent calculation of the binary boundary systems Al-Mg, Al-Si, and Mg-Si (Fig. 1 to 3) together with experimental data for the position of univariant eutectic L $\Leftrightarrow$ α-Al + Mg_2Si in the ternary system. It is of interest to compare the values of thermodynamic parameters used by different authors in the calculation of phase boundaries in this system. For this purpose, we present the values of the interaction parameters at two different temperatures (555 and 595 °C) in Table 1. As can be seen, our interaction parameters have values similar to those used by other authors at given temperatures, thus implying that a rather simple quasi-chemical model is applicable for description of phase equilibria in

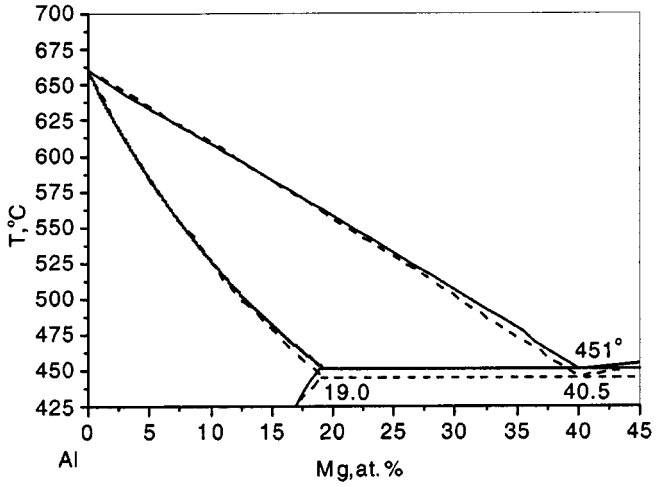

Fig. 1 Fragment of the phase diagram of the Al-Mg system: results of present calculation (solid lines) and data from [1982Mur] (dash lines)

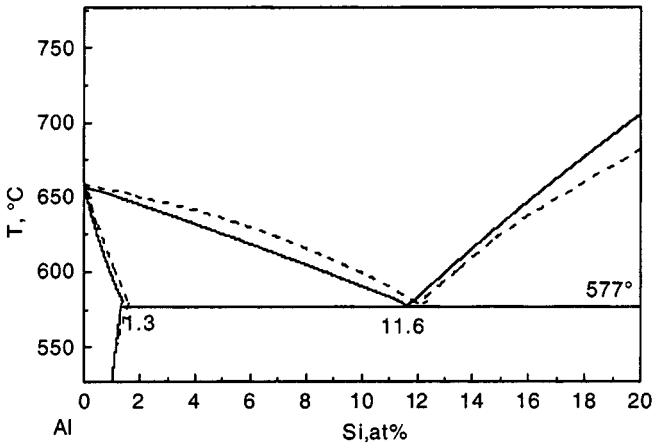

Fig. 2 Fragment of the phase diagram of the Al-Si system: results of present calculation (solid lines) and data from [1986Bar] (dash lines)

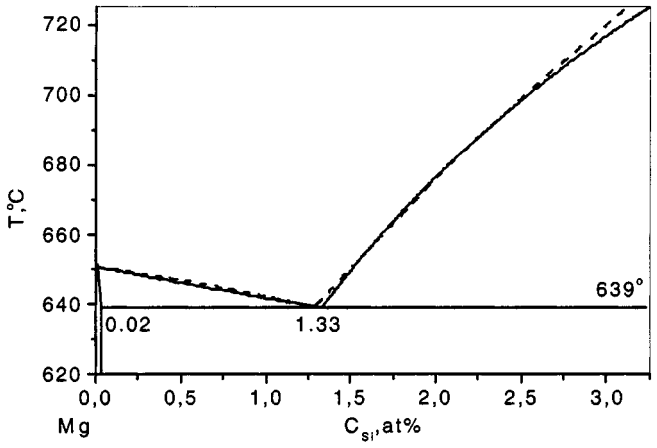

Fig. 3 Fragment of the phase diagram of the Mg-Si system: results of present calculation (solid lines) and data from [1986Lüd] (dash lines)

the Al-Mg-Si system. We have also varied values of interaction parameters within the wide limits (Table 1). The results established that variation of W^f_{ij} in the limits of Table 1 preserves the characteristic features of the equilibria of the fusion diagram under consideration, *viz.* noncoincidence of the quasibinary section (α-Al + Mg_2Si) with the corresponding stoichiometric section of the ternary system and its displacement to the area of alloys enriched in magnesium. The calculated part of the phase diagram is shown in Fig. 4. It is known that the maximum in the concentration dependence of the eutectic transformation temperature is determined by the condition of contact of two respective liquidus surfaces (L $\Leftrightarrow$ α-Al and L $\Leftrightarrow$ Mg_2Si), whereas the actual coordinates of the univariant eutectic transformation L $\Leftrightarrow$ α-Al + Mg_2Si are defined by the condition of their crossing. The L $\Leftrightarrow$ α-Al surface is asymmetric with respect to the stoichiometric section Al-Mg_2Si, which is induced by different solubility of magnesium and silicon in the aluminum melt. As a result, the point e^o, which is a contact point between the respective isotherms of liquidus (L $\Leftrightarrow$ α-Al and L $\Leftrightarrow$ Mg_2Si), is displaced to the area of alloys enriched in magnesium. The contact of the two liquidus curves (L $\Leftrightarrow$ α-Al and L $\Leftrightarrow$ Mg_2Si) occurs at 591 °C, while the ratio of the components C_{Mg}/C_{Si} in the alloy equals 2.51. Various stages in the calculation of fusion diagram are shown in Fig. 5. The quasi-binary section (α-Al + Mg_2Si) of the phase diagram is shown in Fig. 6, and the concentration-temperature parameters of the univariant eutectic transformation under consideration are given in Fig. 7.

3. Experimental Results

The experimental investigation of the phase equilibria was carried out by means of thermal analyses, with microstructure and crystallography being studied with optical and electronic microscopes (Fig. 8 and 9). The alloys were melted in alumina crucibles under flux. Then, the alloys were cast in a copper mold with a diameter of 20 mm; casting was immediately followed by quenching in water. The thermal analyses of the alloys were carried out using the Stokes method [1990Bar], with constant thermal flow to the sample and stabilization of cold thermocouple junctions providing precise determination of the temperatures of phase transformations and intervals of their occurrence within ±10 and ±2 °C, respectively. A significant number of alloys with various structures were prepared, some of which are presented in Fig. 10.

It is established that the line of univariant eutectic equilibrium L $\Leftrightarrow$ α-Al + Mg_2Si is described by the expression $\ln(C_{Si}) = -8.545 - 2.266 \cdot \ln(C_{Mg})$, with the dispersion of experimental data $\sigma^2 = 1.235 \cdot 10^{-3}$, where C_{Si} and C_{Mg} are the concentrations (at.%) of silicon and magnesium, respectively. Coordinates of the point e^o are 9.84% Mg and 3.84% Si (C_{Mg}/C_{Si} = 2.51), with T = 597 °C. The microstructural studies indicate that the eutectic α-Al + Mg_2Si alloys belong to the class of faced-unfaced eutectics. The growth of eutectic colony in these alloys begins with the formation and growth of a faced Mg_2Si crystal, from the top and edge parts of which evolve branches; these give rise to the actual eutectic colony representing a bicrystal formation made of fibers and

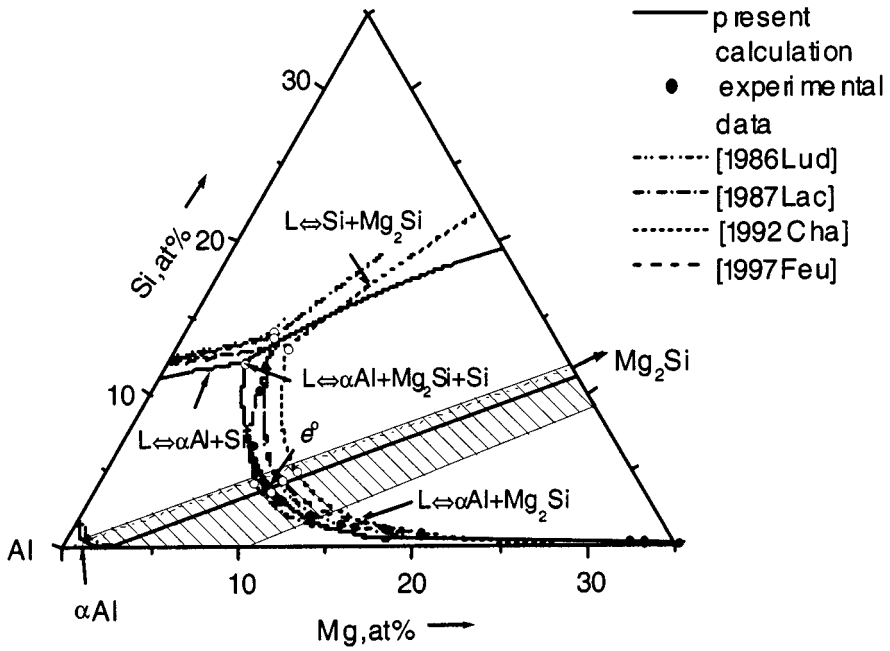

Fig. 4 Fragment of the phase diagram of the Al-Mg-Si system: results of present calculation (solid lines) and experimental results (●). Thick solid line represents the quasi-binary section, and the thin dash line represents stoichiometric section. Shaded area is the calculated area of α-Al + Mg_2Si binary alloys

Table 1 Parameters used for the calculation of the aluminum-rich portion of the Al-Mg-Si phase diagram

Parameter	*T*, °C	[Lud1986]	[Feu1997]	[Cha1992]	Present calculation	Interval of variation of the parameter
$F_{Al}^{\alpha \to L}$, J · mol^{-1}	555	1,411	…	1,222	1,189(a)	
	595	939.2	…	757.1	729(a)	…
$F_{Mg}^{\alpha \to L}$, J · mol^{-1}	555	−2,527	…	−991	−2,514(a)	…
	595	−2,984	…	−1,317	−2,974(a)	…
$F_{Si}^{dia \to L}$, J · mol^{-1}	555	−55,000	…	25,770	23,598(b)	…
	595	−56,200	…	24,570	22,485(b)	…
$F_{Si}^{\alpha \to L}$, J · mol^{-1}	555	−6,749	…	−7,180	−6,749(b)	…
	595	−7,228	…	−7,508	−7,228(b)	…
W_{AlMg}^{L}, J · mol^{-1}	555	−4,909	−4,231.1	−4,909	−2,570	−1,285/−3,855
	595	−5,025	−4,006	−5,025		
W_{AlMg}^{fcc}, J · mol^{-1}	555	− 1,519	4,167	1,519	3,406	1,703/5,109
	595	− 1,029	4,137	1,029		
W_{AlSi}^{L}, J · mol^{-1}	555	−13,000	−12,959	−12,820	−9,404	−14,106/−4,702
	595	−12,850	−12,830	−12,670		
W_{AlSi}^{fcc}, J · mol^{-1}	555	−5,894	−2,818	−3,700	1,574	332/2,361
	595	−5,998	−2,803	−3,717		
W_{MgSi}^{L}, J · mol^{-1}	555	−54,860	−57,069	−49,360	−50,972	−76,458/−25,486
	595	−56,770	−55,771	−49,230	−41,812	−62,718/−20,906
W_{MgSi}^{fcc}, J · mol^{-1}	555	…	−6,409	−996	−28,470	−42,705/−14,235
	595	…	−6,373	−978	−27,590	−41,385/−13,795
W_{AlMgSi}^{L}, J · mol^{-1}	555	−106	3,444	−72	…	…
	595	−82	−560	−36	…	…
G_{Mg2Si}, J · mol$^{-1}{}_i$	555	−52,040	−50,110	−48,420	−82,872	−102,440/−77,336
	595	−53,970	−52,126	−50,380	−73,696	−93,403/−68,298

(a) Parameters from [Kau1972]
(b) Parameters from [Whi1965]

platelets of Mg_2Si, regularly distributed in the aluminum matrix (Fig. 9).

The temperatures of the beginning and completion of melting of the alloys with compositions located along the line of

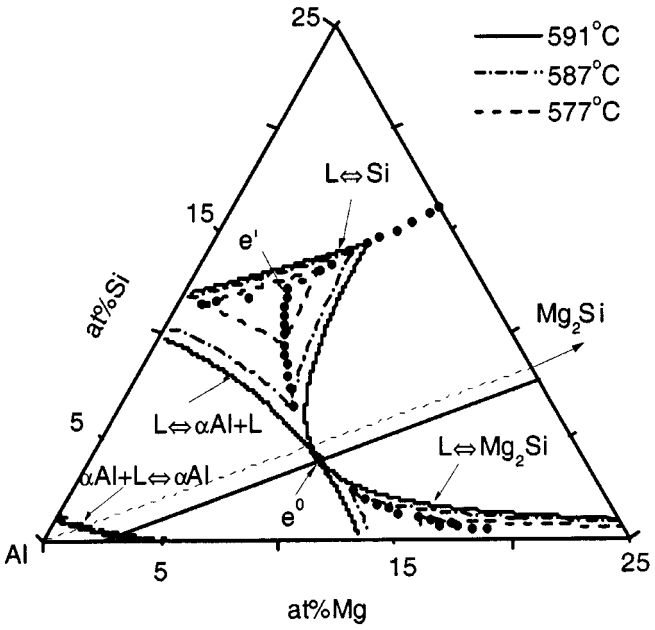

Fig. 5 Coordinates of the univariant eutectic transformations L ⇔ α-Al + Mg_2Si, L ⇔ α-Al + Si, and L ⇔ Si + Mg_2Si, defined by the condition of crossing of two respective liquidus surfaces (●). Point e^o: the point of contact between the isotherms of liquidus (L ⇔ α-Al and L ⇔ Mg_2Si), and point e': the composition of eutectic L ⇔ α-Al + Mg_2Si + Si alloy. Thick solid line represents the quasi-binary section, and thin dash line represents the stoichiometric section

univariant eutectic equilibrium L ⇔ α-Al + Mg_2Si are shown in Fig. 11.

The regions of binary alloys after crystallization and after high-temperature annealing were studied. The boundaries of the area of binary (α-Al + Mg_2Si) alloys were determined by means of differential thermal analysis. For this purpose, the alloys with compositions located along the line of univariant eutectic transformation L ⇔ α-Al + Mg_2Si to both sides of the quasi-binary section were annealed beforehand for 30 min at temperatures some 15 °C higher than the melting temperatures of the corresponding ternary eutectics (L ⇔ α-Al + Mg_2Si + Si and L ⇔ α-Al + Mg_2Si + Al_3Mg_2). In the alloys with compositions falling at the boundaries of the binary (α-Al + Mg_2Si) region, the traces of the third phase were observed and a peak corresponding to the melting temperature of one of the ternary eutectics (445 and 555 °C) appeared in the cooling curve. Note that these alloys have the maximum eutectic melting range. The binary (α-Al + Mg_2Si) region is located within the limits of 2.1 to 8 of the component ratio (C_{Mg}/C_{Si}) in eutectic alloys. There is good agreement between the experimentally measured and the calculated boundaries of the two-phase area (α-Al + Mg_2Si).

The boundaries of the area in the fusion diagram that represents a set of binary (α-Al + Mg_2Si) at crystallization alloys were determined experimentally by means of structural investigation and thermal analysis of the cast alloys (Fig. 11). The position of this area in the ternary system is an important technological factor, which determines possible compositions of the alloys not containing an easily melted ternary eutectic L ⇔ α-Al + Mg_2Si + Si (Fig. 8a)

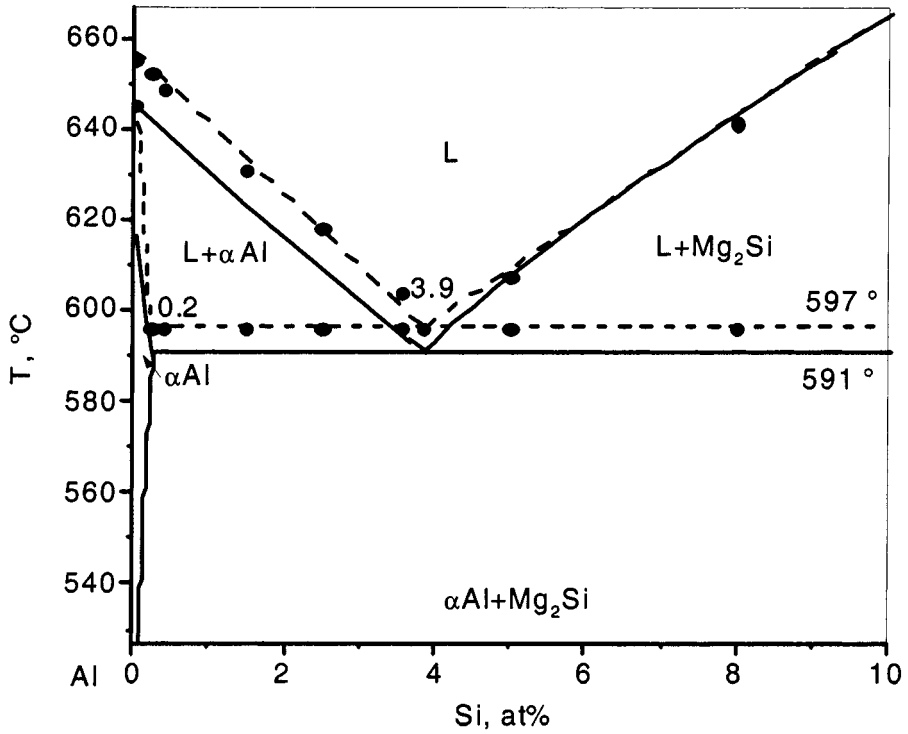

Fig. 6 Quasi-binary section of the phase diagram of the Al-Mg-Si system: experimental results (●) and results of present calculation (solid lines)

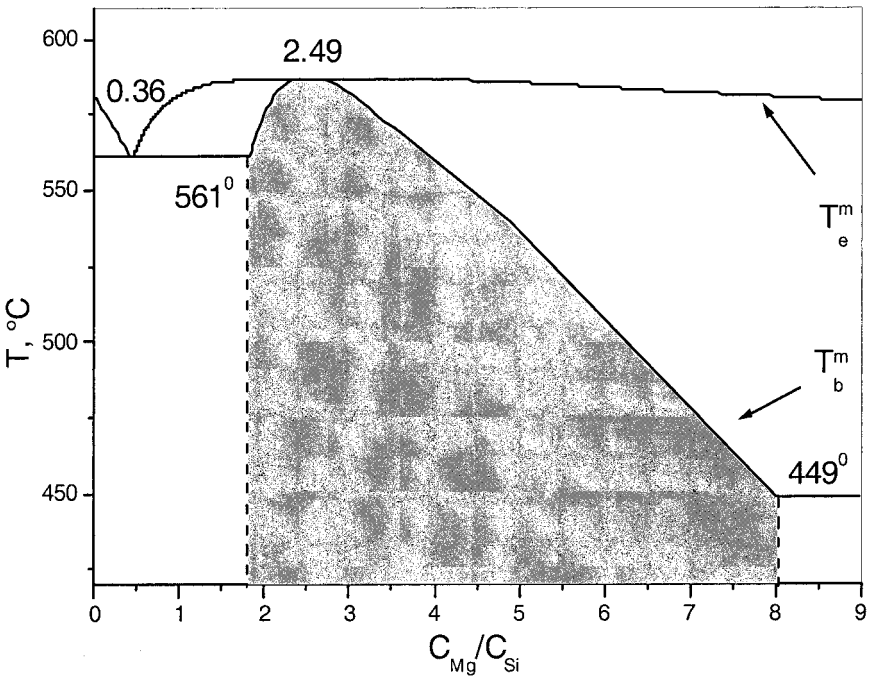

Fig. 7 Calculated concentration-temperature parameters of the univariant eutectic equilibrium L ⇔ α-Al + Mg_2Si. The gray area represents the calculated region of α-Al + Mg_2Si binary alloys. T^m_b and T^m_e are temperatures of the start and completion of melting of the alloys with compositions located along the line of univariant eutectic equilibrium L ⇔ α-Al + Mg_2Si

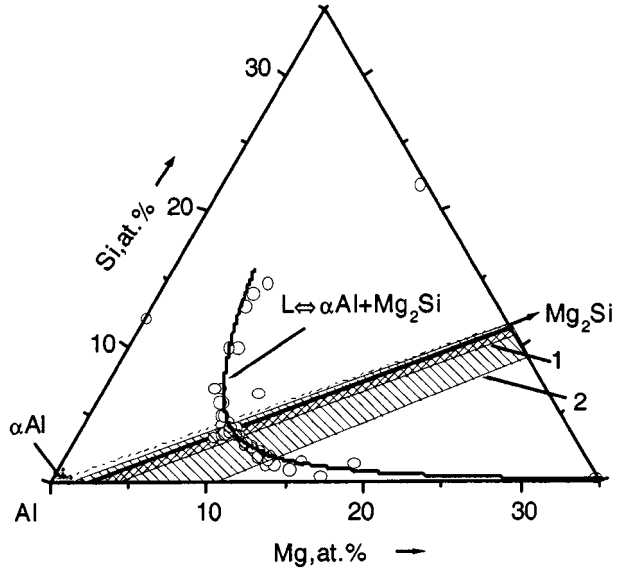

Fig. 8 Fragment of the phase diagram of the Al-Mg-Si system: experimental lines of the invariant eutectic transformations L ⇔ α-Al + Mg_2Si (solid lines) and selected alloy compositions (◦). Thick solid line represents the quasi-binary section, and thin dash line represents stoichiometric section. 1—area of α-Al + Mg_2Si binary alloys, and 2—area of α-Al + Mg_2Si binary at crystallization alloys

or L ⇔ α-Al + Mg_2Si + Al_3Mg_2 (Fig. 8c) in their structure after casting. It is established that the specified area is located within the limits of 2.2 to 3 of the component ratio (C_{Mg}/C_{Si}) in eutectic alloys.

The experimental investigation of the position of liquidus surfaces (L ⇔ α-Al and L ⇔ Mg_2Si) allows determination of the volumetric fraction of Mg_2Si in the eutectic alloy on the quasi-binary section (having the maximum melting temperature and zero melting range) with high accuracy. Such studies established that the eutectic contains about 13.10% Mg_2Si on the quasi-binary section. The results of all thermodynamic calculations of the lines of univariant eutectics (L ⇔ α-Al + Mg_2Si, L ⇔ α-Al + Si, and L ⇔ Si + Mg_2Si) are presented in Fig. 4 together with the experimental results. The direct comparison provides evidence of large informative capabilities of the quasi-chemical phase model for the description of the fusion diagrams of aluminum alloys.

4. Conclusions

- The location of the line of univariant eutectic equilibrium L ⇔ α-Al + Mg_2Si in the ternary system was determined and its analytical expression was proposed.
- It was established that the area of binary (α-Al + Mg_2Si) alloys is displaced relative to this section toward the area of magnesium-enriched alloys. It is noted that, in the cast alloys not subjected to thermal treatment, this area significantly converges and does not extend to the stoichiometric section Al-Mg_2Si of the fusion diagram of the ternary Al-Mg-Si system.
- The characteristic features of the fusion diagram of the system of alloys Al-Mg-Si (displacement of the quasi-binary section (α-Al + Mg_2Si) relative to the corresponding stoichiometric section and the extension of the binary

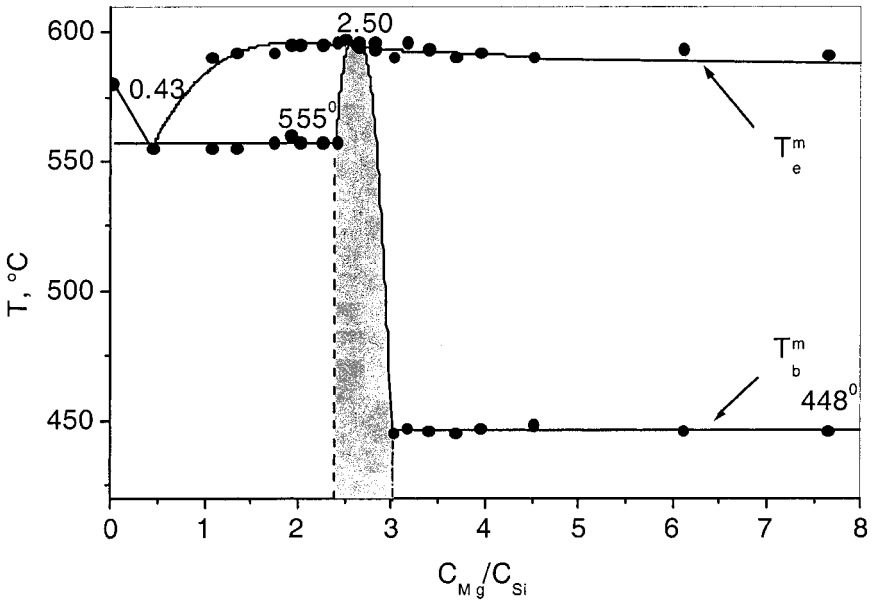

Fig. 9 Conditions for occurrence of eutectic transformation L ⇔ α-Al + Mg_2Si in the Al-Mg-Si system: experimental data (●). The gray area represents the region of the α-Al + Mg_2Si binary at crystallization alloys. T^m_b and T^m_e are temperatures of the beginning and completion of melting of the alloys with compositions located along the line of univariant eutectic equilibrium L ⇔ α-Al + Mg_2Si

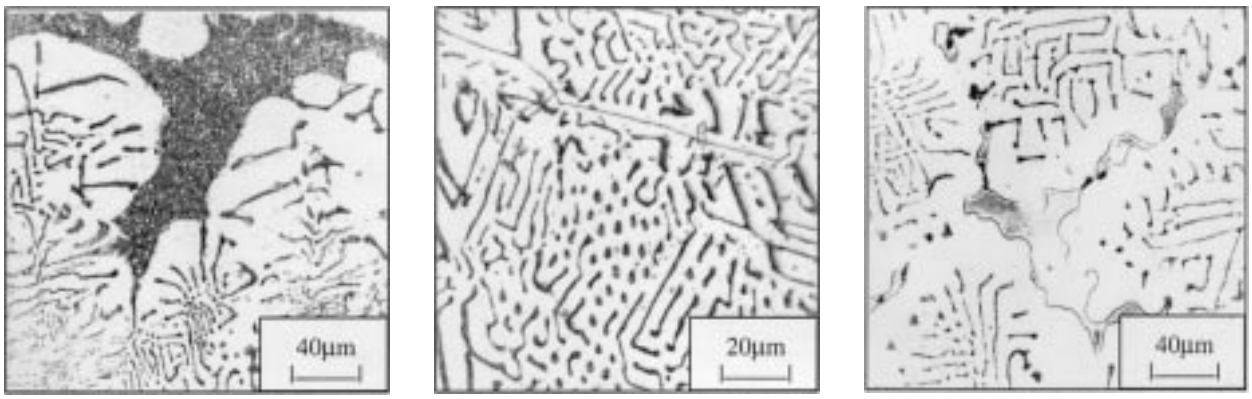

Fig. 10 (**a**) to (**c**) The characteristic microstructures: (**a**) (α-Al + Mg_2Si) + (α-Al + Mg_2Si + Si), (**b**) (α-Al + Mg_2Si), and (**c**) (α-Al + Mg_2Si) + (α-Al + Mg_2Si + Al_3Mg_2)

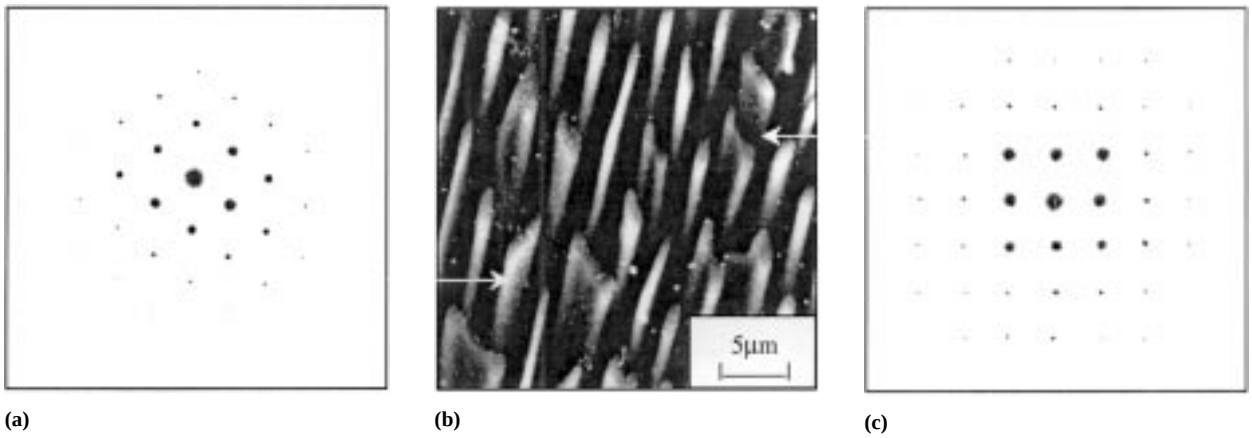

Fig. 11 (**a**) to (**c**) Electron diffraction patterns (**a**) from the α-Al matrix and (**c**) from the Mg_2Si fibers in the eutectic alloy α-Al + Mg_2Si. (**b**) The structure of the eutectic alloy α-Al + Mg_2Si (α-Al matrix is removed by selective etching)

area (α-Al + Mg_2Si) to the compositions of alloys enriched in magnesium) are a consequence of the asymmetry of liquidus surface L $\Leftrightarrow$ α-Al, induced by different solubility of magnesium and silicon in the aluminum melt. The same features in the fusion diagram may be predicted for other similar systems as well (*i.e.*, for the system of alloys Al-Mg-Ge).

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